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Preparation of MnZn-ferrite with microemulsion technique

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Abstract

Nanocrystalline MnZn-ferrite particles with different morphology were prepared from single water-in-oil microemulsion consisting of n-hexanol as an oil phase, surfactant CTAB and an aqueous solution of mixed metal sulfates. A sodium hydroxide solution was used as the precipitating agent and a hydrogen peroxide as the oxidizing reagent. The synthesized materials were characterized using an X-ray diffraction (XRD), transmission electron microscope (TEM), BET surface analyzer and magnetometry.

Keywords: Ferrites; Nanoparticles; Magnetic properties; Powders-chemical preparation; Soft magnets

1. Introduction

Manganese zinc ferrite ceramics play an important role in the area of electronic materials. Due to their outstanding magnetic properties, particularly high magnetic polarisability and high electric resistivity, they are widely used in numerous electronic and magnetic applications.[1] Particularly, when dealing with power ferrites, development of fine-grained microstructure is of a crucial importance.[2] The study, development and application of small agglomerate free powders is one of the important tasks in the preparation of manganese zinc ferrite ceramics.

There are several methods of preparation of fine-powder including hydrothermal synthesis,[3] precipitation/coprecipitation,[4] sol-gel processes[5] etc. Among these processes, precipitation in a microemulsions has lately shown to be a very promising technique for the preparation of ultrafine ferrite particles[6] of controlled size and morphology with a number of application. In this method, a surfactant [S] is dissolved in organic solvents which form spheroidal aggregates, named reverse micelles. It is known that the reverse micelles are in fact a water-in-oil microemulsions where tinny droplets of water are surrounded by surfactant molecules forming a so called "water pools", which are characterized by water-surfactant molar ratio, $w = [H_2O]/[S]$. Water pools of these reverse micelles act as micro-reactors for the synthesis of MnZn-ferrite powders, in which the particles size of the product is controlled by the size of these pools.[7]

The purpose of this study was to synthesize the magnetic MnZn-ferrite nanoparticles using microemulsion technique and to examine the conditions which modify the particle morphology.

2. Experimental

To select a proper composition that would form reverse micelles, a phase diagram water/CTAB/n-hexanol[8] was used. The microemulsion system consisted of n-hexanol as an oil phase, n-hexadecil trimethylammonium bromide (CTAB) as a surfactant and an aqueous phase of metal salts. Aqueous solution containig Fe^{2+}, Mn^{2+} and Zn^{2+} ions was prepared by dissolving an appropriate amount of metal sulfates (1.0 M $FeSO_4$, 0.25 M $MnSO_4$ and 0.25 M $ZnSO_4$) in deionized water which resemble to the ferrite stoichiometry. Aqueous solution of 6N NaOH served as a precipitating agent. The compositions as shoved in the phase diagram (Fig. 1) were prepared by mixing of an appropriate amount of water solution of metal sulfates with proper amounts of CTAB and n-hexanol. During mixing, the microemulsion was heated and kept at temperature between 50 and 60 °C. When an alkaline solution of 6N NaOH was added to the starting microemulsion, the pH

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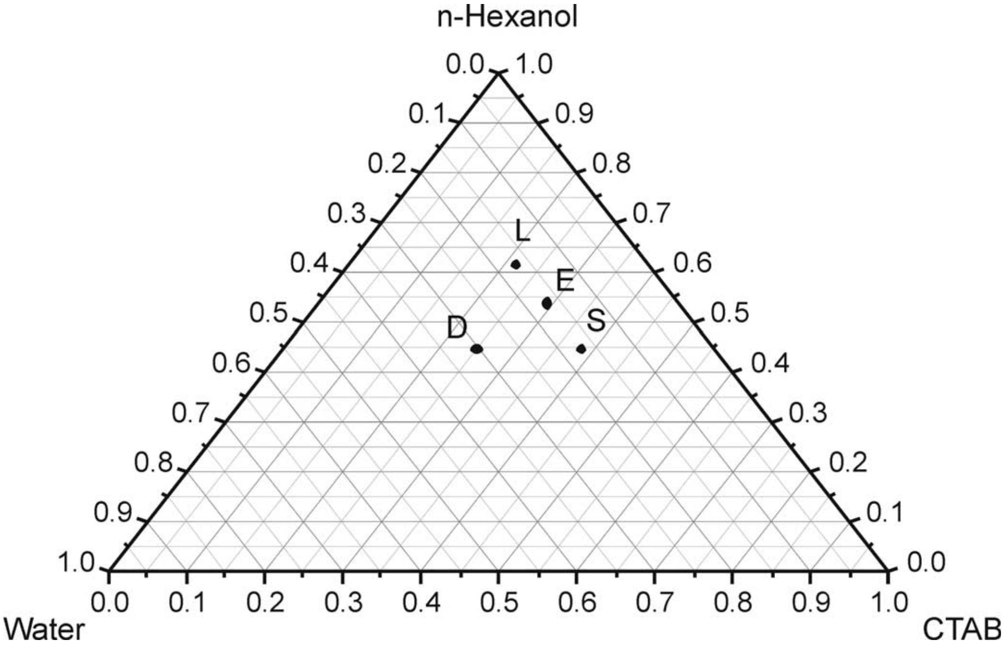


Fig. 1. The phase diagram investigated with phase composition examined.

value rose to about 11 and an intermediate precipitate was formed. As oxidation took place, intermediate precipitate was changed into the precipitate of the spinel phase. A 30% solution of hydrogen peroxide was used as the oxidizing reagent. The resulting microemulsion was then mixed with an equal volume of water–methanol (1:1) solution to break up the micelles by washing the particles. The samples were then centrifuged followed by further washing this particles several times using ethanol and dried at 70 °C. After the samples were centrifuged, the residue obtained was analysed in order to monitor the possible leaching of Zn^{2+} ions. In spite of the relative high pH value of the solution, a significant Zn^{2+} ions weren't present (<5 mg/l).

The process of formation of the MnZn-ferrite spinel by hydrolyzing and oxidizing of alkaline $Fe(OH)_2$ suspensions mixed with Mn^{2+} and Zn^{2+} ions at elevated temperatures is based on the Schikorr's reaction.[9] In our experiments the reaction proceeds in "water pools" provided by reverse micelle technique and is governed by the oxidation of hydrolized mixture of an appropriate composition in an alkaline media:

$$x\mathrm{Mn}^{2+} + y\mathrm{Zn}^{2+} + (3\text{-}x - y)\mathrm{Fe}^{2+} + 6\mathrm{OH}^- + 1/2\mathrm{O}_2$$

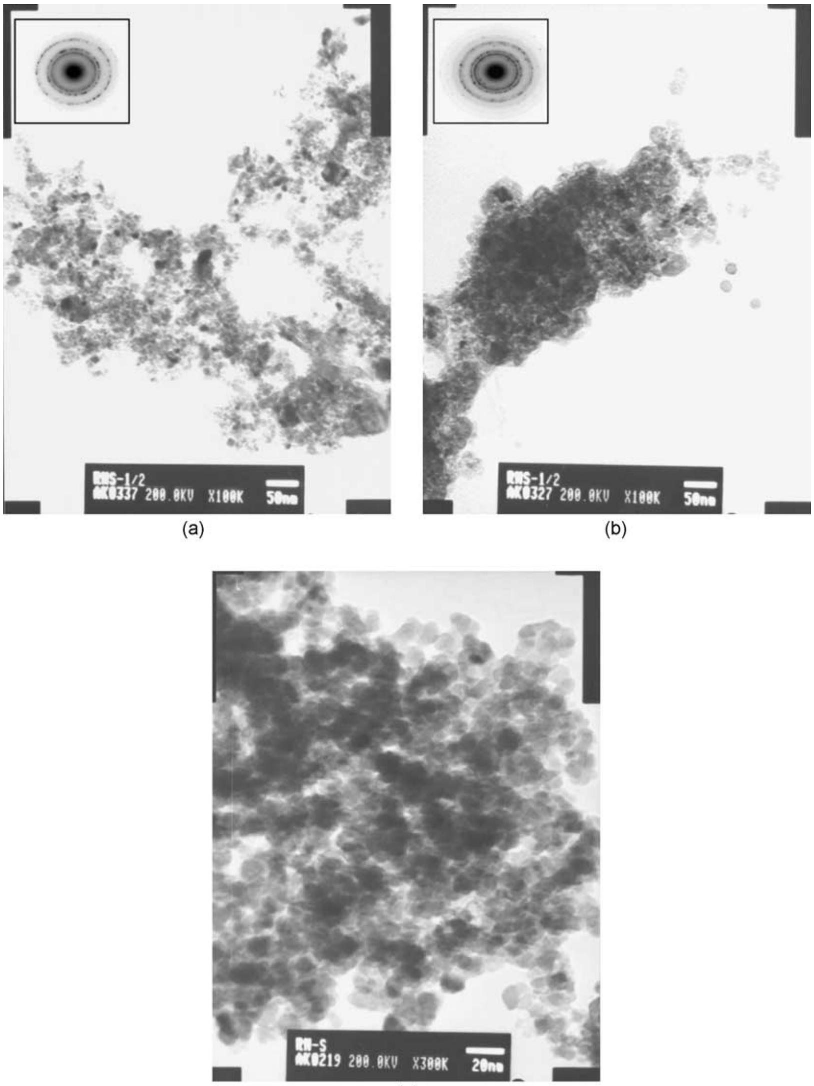
$$\Rightarrow \mathrm{Mn}_x\mathrm{Zn}_y\mathrm{Fe}_{3-x-y}\mathrm{O}_4 + 3\mathrm{H}_2\mathrm{O}$$

The synthesized powders were examined by an X-ray diffraction spectroscopy to identify the powders. The particle size was determined from the (311) diffraction line broadening using Scherrer method.[10] The morphology of the individual grains of ferrite was examined using transsmision electron microscope (TEM). Specific surface area of powders was determined by BET method. The magnetic properties of powders were measured using a vibrating sample magnetometer. Powders were also characterized using thermogravimetric (TGA) and differencial thermal analysis (DTA).

3. Results and discussion

Phase diagram as exhibited in Fig. 1 shows the compositions L, E, S and D, which were selected in accordance with the phase diagram water/CTAB/n-hexanol.[8] These compositions were examined and exposed to a more detailed analyses.

The changes in the individual grain size of particles prepared from the composition marked L,E,S and D were examined on the basis of the CTAB/n-hexanol ratio. It is generally known that the water/surfactant ratio (w) is a cruicial parameter that governs the size of water droplets—"water pools" in an oil continuum. During the course of this work the H_2O/CTAB (w) ratio was changed by changing the CTAB/n-hexanol ratio. An increase in this ratio has an indirect influence on the w in the phase diagram. The increase of the CTAB/n-hexanol ratio causes no detectable change in the particles size. It is expected that an increase in the CTAB/n-hexanol ratio with simultaneous decrease of w, would cause a decrease in the average particle size of precipitated powders. The change in the particle size, as observed in the samples L, E and S was relatively small.



(a) (b)

(c)

Fig. 2. (a) TEM image of microemulsion derived MnZn ferrite particles obtained from the microemulsion with composition D. (b) TEM image of microemulsion derived MnZn ferrite particles obtained from the microemulsion with composition S. (c) TEM image of microemulsion derived MnZn ferrite particles obtained fom the microemulsion with composition L.

The variation of CTAB/n-hexanol was found to have only a limited affect on the average particle size of the powders synthesized from the composition L, E and S with a constant water content. On the other hand, when the *w* and the water amount were increased from E to D the average particles size was found to increase. An exception was powder S, where the average particle size determined from the specific surface measurments showed a much higher average particle size in comparison to that determined from X-ray diffraction line broadening (Fig. 3). However, this can be explained by an intensive agglomeration of powder S obtained from the composition with the highest amount of surfactant (Fig. 2b). The morphology of the ferrite powders synthesized with the compositions L, D and S with the corresponding diffraction patterns are shown in Fig. 2a–c.

The electron diffraction pattern indicated that the ferrite powders as obtained by this method were crystalline. The properties of the samples obtained at different CTAB/n-hexanol weight ratios and their various morphologies, are given in Table 1.

Table 1
Composition of microemulsions, specific surface area (A_s), average particle size obtained from specific surface area (d_A), average particles size obtained from XRD (d_x) and specific magnetization (σ)

Sample	CTAB/n-hexanol (weight ratio)	A_S (m^2/g)	d_S (nm)	d_X (nm)	σ_S (emu/g)
S	0.84	46.6	25	9.4	8.1
E	0.53	156.6	7	7.5	8.9
L	0.32	119.1	10	9.0	9.1
D	0.54	106.7	11	14.1	14.3

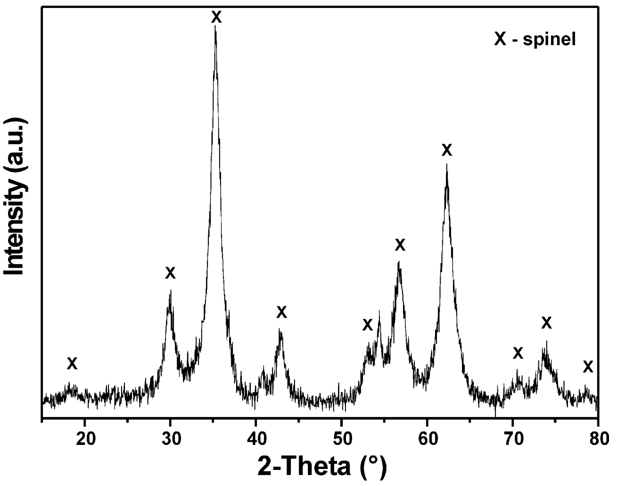


Fig. 3. XRD pattern of microemulsion derived MnZn ferrite powders.

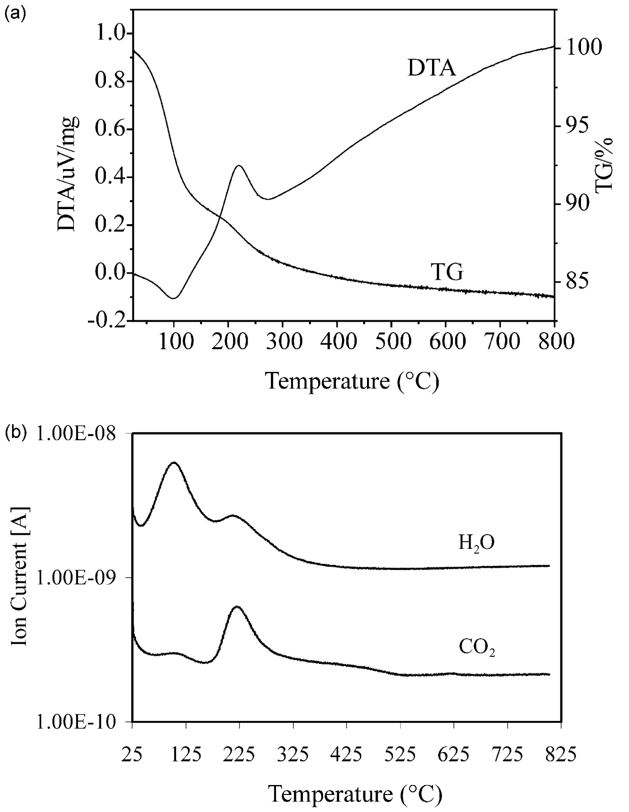


Fig. 4. (a) TGA and DTA curves of microemulsion derived MnZn-ferrite powder. (b) Mass spectrum of microemulsion derived MnZn-ferrite powder.

Fig. 4a shows the TGA and DTA curves for the microemulsion derived ferrite powder at a heating rate of 10 °C/min from room temperature to 800 °C. TGA curve shows two areas of weight loss, first is over the temperature range from room temperature to 100 °C and the second is over the temperature range from 120 to 300 °C. The first weight loss indicates the loss of residual solvent and water in as-dried precursor powder. The second weight loss is due to the decomposition of surfactant CTAB. This is further confirmed by the occurance of endothermic (evaporation of water) and an exotermic peak (oxidation of hydrocarbons) on the DTA curve in combination with mass spectroscopy (Fig. 4b).

4. Conclusions

Precipitation in microemulsions of manganese zinc ferrite powder yields a nanosized crystalline powder with relatively uniform particle size distribution. It was found that the CTAB/n-hexanol weight ratio affects on the particles size. In the powders synthesized in presence of a surfactant, a strong powder agglomeration was observed. A larger particles size of the powders thus synthesized causes an increase of specific magnetization.

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